Innovative Techniques for the Production of Energetic Radicals for Lunar Materials processing Including Photogeneration Via Concentrated Solar Energy

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Abstract

In the previous progress report for 1989-90, a technique was discussed for photo generation of radicals that can be used in the recovery of oxygen and metals from extraterrestrial resources. This report is a continuation of that discussion, but is focused on the progress that has been achieved in the past 12 months. During that period it was necessary to move the equipment from the Arizona Materials Laboratories to the Solar Energy Research Facility at the main campus of the University of Arizona. In spite of that delay we have conducted a number of experiments and have achieved significant results.

Introduction

This program is funded by the Space Engineering Research Center, the Arizona Mining and Minerals Resources Research Institute (Grant # G1104104) and the Solar Energy Research Facility. We gratefully acknowledge their support. Because of the nature of the present funding we have submitted a pre-proposal to the Solar Energy Research Institute in Golden, Colorado and a full proposal to the U. S. Bureau of Mines for continuation of this work.

The concept behind this work has been to examine methods whereby radicals can be generated and used in the processing of refractory materials. In that regard we have focused on the use of sunlight. Sunlight provides useful energy for processing in the forms of both thermal and quantum energy. While the use of thermal energy is well accepted, the use of quantum energy of the solar photons (photonic processes) for chemical reactions presents new and exciting possibilities.

Light can affect materials thermally or through photonic processes. the absorption of light can lead to an increase in the vibrational, rotational, and translational energy of the atoms of the material. This shows up, macroscopically, as an increase in temperature and, once absorbed, the effectiveness of the energy is not dependent on the wavelength of light. Photonic processes are

wavelength dependent and are characterized by a threshold wavelength that is specific for each process and material.

If light is absorbed by a molecule and it has sufficient energy, it can cause a transition of electrons from one orbital to another. If the electron belongs to a chemical bond, the bond may be broken by this transition. Ultra violet (UV) and near UV radiation, as the most energetic portion of the solar spectrum, can break a wide variety of bonds, including that of diatomic chlorine. It is that potential which is the focus of the present investigation.

Photo enhanced chlorination could be used to separate metals from complex alloys such as that which might be produce in in situ electrolysis of Lunar regolith. Or it might also be possible to use solar energy in the chlorination and/or carbochlorination of metal oxide to produce oxygen.

A number of researchers have examined the chlorination kinetics of metals, metal oxides and metal sulfides. Certainly the most extensive and through work has been conducted by Dr. A. Landsberg at USBM's Albany, Oregon Research Center (1 - 6).

Dr. Landsberg found that the chlorination kinetics of both metals and metal oxides involves two separate processes that can be distinguished by the order of their dependence on the partial pressure of Cl_2. In all instances the order has been found to be either 1/2 or 1 depending on the temperature of reaction. The 1/2 power suggests that the splitting of diatomic chlorine is involved in the rate limiting step.

The chlorination of a metal can, in general, be represented by the following reaction:

$$M(s) + \quad \begin{cases} xCl_2 \longrightarrow \!\!\!\wedge\!\!\wedge\!\!\wedge\!\!\wedge \\ 2xCl \longrightarrow \!\!\!\wedge\!\!\wedge\!\!\wedge\!\!\wedge \end{cases} = MCl_{2x} \qquad (1)$$

where M represents any metal. The equation shows that two reaction paths are possible, one involving diatomic chlorine and the other monatomic chlorine. The resistors in the equation serve as reminders that while both reactions proceed in parallel it is expected that the resistance of one of the paths will be so large that it will effectively preclude that mechanism.

Carbochlorination is more complex. Barin and Schuler, however, have provided convincing evidence of the importance of monatomic chlorine in the chlorination of TiO_2 (7). Those workers reacted disks of TiO_2 with and without carbon in the presence of Cl_2 and Cl_2-CO-CO_2 gas mixtures. When the Cl_2-CO-CO_2 gas mixture was used the CO_2/CO ratio was the same as in the Boudouard equilibrium for the particular temperature under investigation. The chlorination rates of TiO_2 without solid carbon, but with the CO_2-CO gas mixture, was several orders of magnitude less than that achieved when solid carbon was present. Since the CO and CO_2 established the same oxygen potential as that achieved with the solid carbon, Barin and Schuler deduced that the carbon activated the chlorine by splitting the diatomic molecule.

To test their theory, Barin and Schuler placed small inert spacers between the disks of carbon and TiO_2. They found that the rate of chlorination decreased as the separation between the carbon and TiO_2 increased. At a separation distance of $20\mu m$ the rate was reduced by half, and at a separation of $100\mu m$ the rate of chlorination was equal to that experienced without solid carbon being present. Barin and Schuler postulated that the probability that monatomic chlorine (formed on the surface of the solid carbon) recombines before reaching the TiO_2 increases with the separation distance.

Experimental Results

A number of experiments have been conducted in the chlorination of metals with and without the aid of UV and near UV light. The results of some of those experiments are discussed below.

In the chlorination of Fe the resistor for the monatomic path in reaction 1 is substantially greater than the resistor involving the diatomic chlorine. The rate of chlorination of iron, unlike many other metals, has been found to be dependent only on the partial pressure of Cl_2 to the first power.

To test the basic hypothesis of the present investigation, namely, that UV and near UV light can be used to generate monatomic chlorine and thereby enhance chlorination rates, identical Fe specimens were reacted in a chlorine containing gas at a fixed pressure. The results of that test are shown in Figure 1. The specimen reacted at 292 °C was exposed to UV and near UV radiation at specified intensities while the specimen reacted at 325 °C was not. The specimen exposed to light reacted twice as fast as the specimen not exposed to light. At 325 °C the rate of chlorination of Fe will double approximately every 15 °C (4). Thus, the rate observed at 292 °C is approximately 800% greater than that which would occur at the same temperature without UV and near UV light.

The increased chlorination rate with UV and near UV radiation can most likely be attributed to augmentation of the total reaction rate by an increase in the rate of chlorination by monatomic chlorine.

These results run counter to those obtained by Landsberg and Block who attempted to use gamma rays to enhance the chlorination rate of metals (4). It is uncertain whether their intent was to activate the metal by radiation damage or to dissociate Cl_2. A gamma ray has sufficient energy to dislodge a proton or neutron from the nucleus of an atom. A gamma ray can dissociate Cl_2 if there is a mechanism to assimilate the large excess energy. If no mechanism exists dissociation will not take place. In essence a gamma ray has too much energy to form monatomic chlorine by a photonic process.

Future Work

The current experimental work involving metals will be continued. We plan, however, to also examine the potential for utilizing solar energy in enhancing both chlorination and carbochlorination of metal oxides, including ilmenite.

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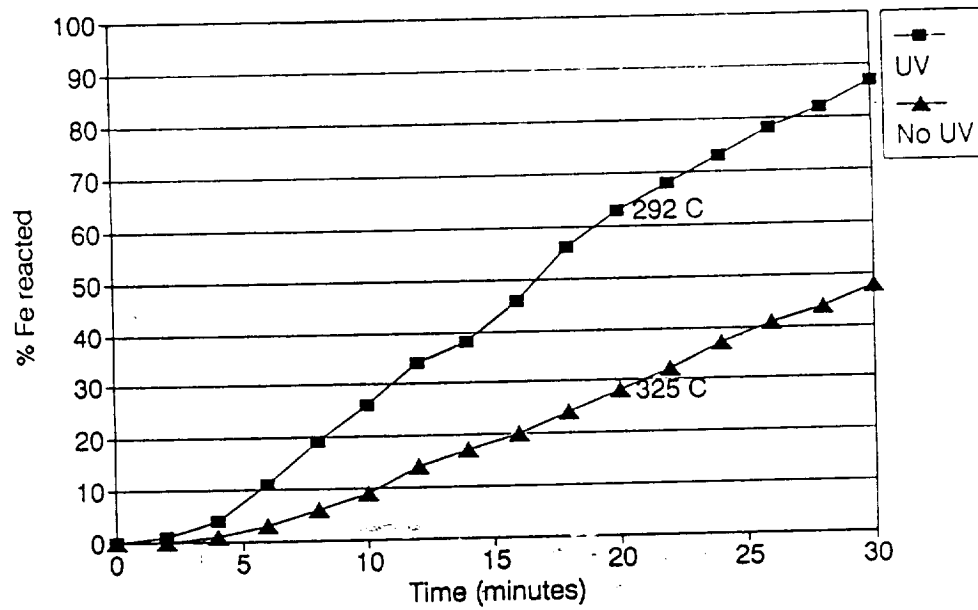# CHLORINATION OF Fe

UV enhanced vs. No UV

Figure 1 - Comparison of reaction results with and without UV and near UV light